

Oxide Matrix Composite by Directional Oxidation of a Commercial Aluminum–Magnesium Alloy

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Oxidation rates of a commercial Al–Mg alloy, Al-5083, were investigated to understand the synthesis of an oxide-based composite. In some experiments, the oxide layer was grown with several platinum wires embedded in the matrix to facilitate transport of electrons. The oxidation rate was not controlled by the rate of transport of the electrons and positive holes through the ceramic oxide layer. In the initial phase of the composite growth, an incubation period was observed due to formation of MgO on the alloy surface. At 1273 K or higher, the incubation period was followed by a period of sustained oxidation after MgO was converted to a spinel layer. It is demonstrated that, after the initial incubation period, the rate of oxidation is influenced by the rate of transport of ions through the oxide matrix composite.

I. Introduction

CERAMIC matrix composites (CMC) are attractive candidates for numerous advanced engineering applications in cutting tools, heat exchangers, engine components, marine hardware, and pumps. In many important areas, they offer crucial advantages over both metals and ceramics. It is well known that several nearly pure metals as different as aluminum and tin can be continuously oxidized in air under controlled conditions to form a growing oxide layer. However, before the discovery of Newkirk *et al.*,^{1,2} directional oxidation did not receive much attention and was not used for the synthesis of useful composite materials. The synthesis of CMC materials involves reaction of bulk liquid metal/alloy with a gas to produce a solid ceramic body by means of a directional growth process.^{1–11} In a manner similar to the directed oxidation of aluminum and tin, several metals such as titanium, zirconium, and silicon form nitrides⁴ when exposed to forming gas containing 96% N₂ and 4% H₂. For each system, there appears to be a range of temperature where the growth rates are high. Outside this temperature range, the growth rates decrease sharply and the CMC synthesis becomes impractical. The composites made at the low end of this temperature range have a low ceramic-to-metal ratio in the body of the composite and vice versa. Thus, the composition and structure of the composites can be controlled, to a certain extent, by controlling the reaction temperature, gas composition, and time.

If pure aluminum is oxidized, it forms a relatively thin oxide coating, and the underlying metal is effectively protected from further oxidation. To avoid such a behavior during preparation of composites, small amounts of dopants are commonly used.³ Additions of magnesium, silicon, germanium, lead, and tin have been used for the synthesis of alumina-based composites.

Nagelberg¹⁰ has shown that magnesium is a critical dopant for directional oxidation. Sindel *et al.*¹² have indicated that the presence of Mg in the alloy is essential for the characteristic directed metal oxidation process to take place. Breval *et al.*¹³ have studied the microstructure and composition of alumina/aluminum composites made by the directed oxidation of an aluminum alloy. They concluded that the ceramic structure is made up of continuous networks of alumina and the aluminum alloy, and some isolated inclusions of the alloy. The importance of the alloy–oxide wetting in the composite growth process has been emphasized in several recent studies.^{14–18} Weirauch¹⁴ has shown that alloying Al with Mg generally improves wettability between the alloy and the oxide. However, wetting is strongly influenced by the experimental conditions. Banerjee *et al.*¹⁵ have pointed out that the dopants used to promote wetting may either reduce the liquid surface tension, decrease the solid–liquid interfacial energy, or induce reactions at the solid–liquid interface. The growth rate is crucially dependent on the alloy composition and temperature.

There is considerable evidence in the literature^{19–21} that, during oxidation of a liquid metal covered by an oxide layer, the oxidation rate is often determined by the rate of transport of an electronic species, i.e., electrons and/or positive holes through the oxide layer. For example, the oxidation rate of liquid lead covered by molten lead silicate can be significantly enhanced, by about an order of magnitude, by electrical short circuiting of the lead silicate melt.^{19,20} The role played by the transport of electrons and ions through the oxide matrix in the composite growth has not been investigated.

In this study, the rates of oxidation of a commercial Al–Mg alloy, Al-5083, are investigated. In some experiments, the oxide layer was grown with 10 platinum wires embedded in the matrix to facilitate transport of electrons and/or positive holes through the CMC layer. The roles played by the transport of electrons and/or positive holes through the ceramic matrix, the metal–oxide wetting, and the gas atmosphere are discussed.

II. Procedures

The thermogravimetric setup used for the oxidation study consisted of a Cahn model 1000 automatic recording thermobalance, a high-temperature vertical tube furnace with silicon carbide elements, and arrangements for the metering and supply of high-purity gases. A schematic diagram of the experimental setup is presented in Fig. 1. The balance had a sensitivity of 0.5 μ g, and the measurement accuracy was 0.1% of the recorder range. The reaction tube was of 50-mm internal diameter and had a 25-mm-long equitemperature zone at the center of the furnace. The furnace was equipped with a Eurotherm controller, which regulated the temperature to within ± 5 K. Before conducting each experiment, the alloy sample was placed in a high-purity alumina crucible and suspended from the thermobalance using a platinum chain. The composition of the alloy is indicated in Table I. The alloy contained 5.5 at.% Mg. A cylindrical piece of the alloy having 15.5-mm diameter and 5-mm height was used for oxidation experiments. The diameter of the alloy

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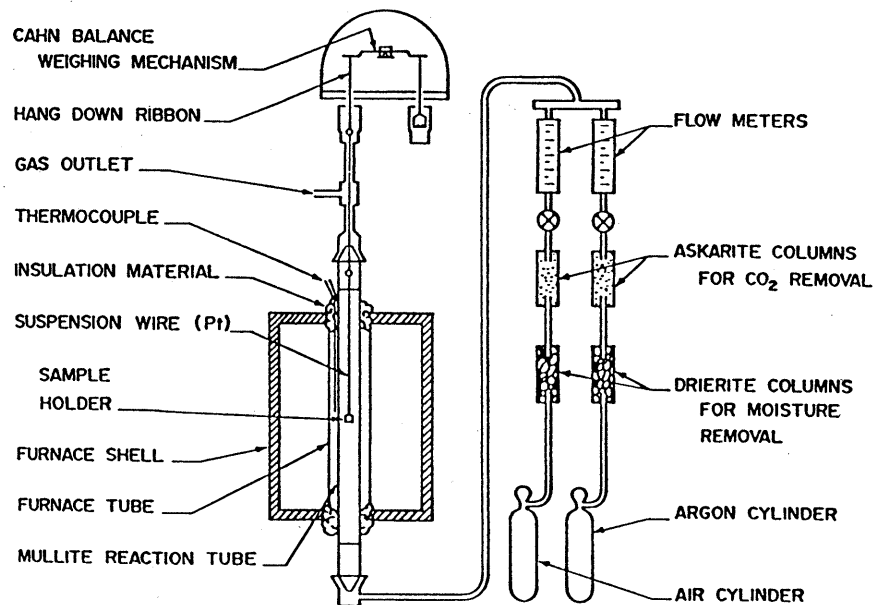


Fig. 1. Schematic diagram of the experimental setup.

block was slightly smaller, by less than 1 mm, than the internal diameter of the crucible. After the sample crucible was inserted in the reaction tube, the tube was purged with argon at a flow rate of 500 sccm for about 20 min. The furnace was then turned on and the sample was heated to the reaction temperature in argon. When the reaction temperature was reached, the argon flow was terminated and a stream of air was introduced into the reaction chamber at a flow rate of 500 sccm. The weight gain vs time data and the furnace temperature were continuously recorded on a strip chart recorder. The oxidation experiments were conducted in the temperature range of 1173 to 1294 K. The average duration of the experiments was about 20 h. The oxidation products were examined using X-ray diffraction and scanning electron microscopy.

III. Results and Discussions

(I) Incubation

During heating of the samples in argon prior to oxidation, some decrease in the weight of the sample was observed at all temperatures, due to vaporization of a small amount of magnesium from the alloy. Magnesium vaporization during heating of Al-Mg alloys is not uncommon.¹⁴ When air was introduced, the weight increased rapidly in the initial period of oxidation. This is observed in Fig. 2 where the weight gain data for the oxidation of the alloy at 1173, 1217, and 1294 K are presented. At 1173 K, the sample gained weight rapidly in the initial period of about 10000 s. In the remaining duration of the experiment, a long incubation period followed, where the rate of weight gain was small. At temperatures higher than 1173 K, the initial

weight gain was followed by an incubation period and, subsequently, a stage of accelerated weight gain was observed.

Although a period of incubation occurred at all temperatures, the incubation period was reduced with the increase in temperature. Cochran *et al.*⁶ have found that, during the initial period of the oxidation of Al-Mg alloys, the melt surface was covered by a layer of MgO, and the accelerated oxidation started only when, at a subsequent time period, spinel formed on the melt surface. In our experiments, X-ray diffraction data of a sample taken from the top crust of a sample oxidized at 1217 K for 3 h showed that the product formed during the incubation period was MgO. The stability of various phases during oxidation of the alloy can be examined on the basis of the Al-Mg-O phase diagrams presented in Figs. 3 and 4. The diagrams were constructed from the available thermodynamic data.^{23,24} The free-energy data used for the calculations and the procedure for the construction of the figures are presented in the Appendix. These diagrams provide a guidance to the sequence of phases to appear as any alloy is oxidized—always assuming equilibrium. It is observed from Fig. 3 that, at 1217 K, the stable product of oxidation of an Al-5 at.% Mg alloy is spinel, which has been observed in the previous work.^{1,2} Furthermore, the range of alloy composition for the formation of spinel widens with increase in temperature, as can be observed from Fig. 4. In the initial stage of oxidation, MgO forms, because magnesium is vaporized from the melt, and the vapor is oxidized close to the melt surface, where the condensed phase rule no longer applies.

Table I. Composition of the Al-5083 Alloy

Element	Composition (wt%)
Al	92.99
Mg	4.84
Mn	0.80
Cr	0.07
Cu	0.09
Fe	0.07
Ti	0.03
Si	0.02

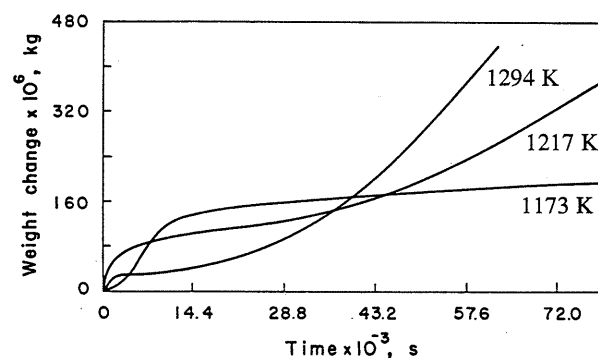


Fig. 2. Weight change vs time plots for Al-5083 alloy in air.

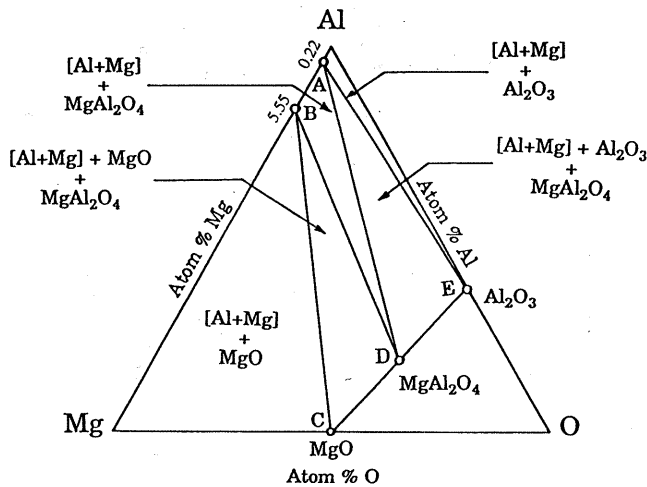


Fig. 3. Calculated isothermal section of Al-Mg-O phase diagram at 1217 K.

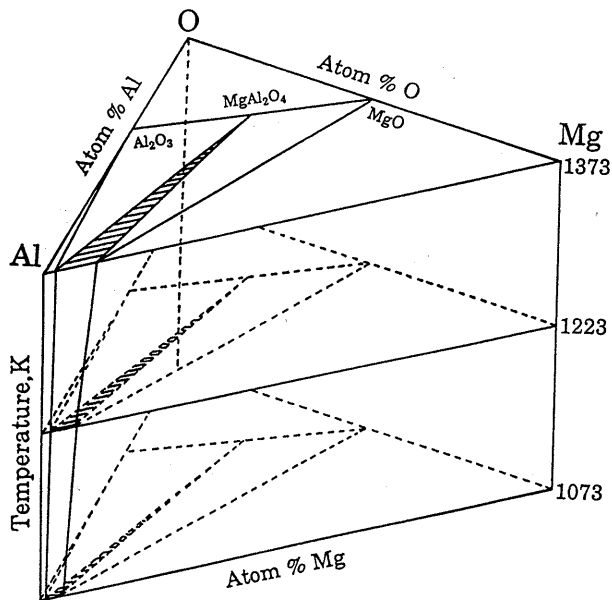


Fig. 4. Three-dimensional representation of the composition-temperature phase relation.

The traditional explanation of incubation is based on the wicking theory, where the oxidation rate depends on the rate of transport of the alloy through the oxide layer. Since the alloy cannot be transported through the MgO layer at high rate, the oxidation rate becomes very slow and an incubation period occurs. However, subsequently, when the spinel forms, the permeation occurs at a high rate in the postincubation period. Since the metal can permeate through the oxide only if the oxide is wetted by the melt, the incubation phenomenon should be examined on the basis of relative wettabilities of MgO and $MgAl_2O_4$. Their relative wettabilities can be examined on the basis of their work of immersion, which is the difference between the solid-liquid interfacial energy, γ_{SL} , and the surface energy of the solid, γ_{SV} . The work of immersion must be negative for the alloy to wet the oxide layer. Since the work of immersion values are not available for the Al-Mg-O system, the contact angle data for the spinel-alloy and the MgO-alloy systems are of interest to examine the relative wettabilities of the two systems. Weirauch¹⁴ has shown that, under identical experimental conditions, a Al-3% Mg alloy has a contact angle

of about 80° with the spinel and about 94° with MgO. Thus, the Al-Mg alloy has higher wettability with the spinel than with MgO. The data are consistent with the fact that during incubation, when MgO forms, the liquid alloy does not wet the MgO layer sufficiently, and the oxidation rate becomes very slow due to poor permeation of the alloy through the oxide. However, when the Al-Mg alloy is kept in contact with MgO for a sufficiently long time, spinel forms in a slow reaction.¹⁴ This reaction signifies some wetting of MgO by the alloy. In the later stages of oxidation, when the spinel forms, the metal permeation improves, due to enhanced wettability, and accelerated oxidation takes place. It is conceivable that, in the initial stages of oxidation, when the composite layer is thin, the alloy can permeate through the composite. However, in a subsequent section of this paper, we will present evidence to demonstrate that the rate of transport of ions influences the growth rate.

(2) Composite Growth

To investigate the role played by transport of electrons through the ceramic matrix, ten platinum wires were positioned inside the Al-Mg alloy so that the wires would be embedded in the composite matrix during oxidation as shown in Fig. 5. These wires short circuit the metal/oxide and oxide/gas interfaces and facilitate transport of electrons during oxidation. The oxidation rates of composites grown with wires are compared with the oxidation rates in control experiments without the platinum wires. At 1217 K, platinum has about 8 at.% solubility in aluminum.²² In some experiments, the crucibles were dissected after the experiments to examine the integrity of the platinum wires. It was observed that the wires remained intact in the ceramic matrix. Furthermore, if the portions of the platinum wires dipped in the alloy were completely dissolved, the resulting alloy would have had only 0.9 at.% platinum. Thus, the alloy composition was not significantly altered during oxidation. The results of oxidation experiments with and without the platinum wires are presented in Fig. 6. Clearly, no significant change in the oxidation rate is observed in the two cases. Thus, the transport of electronic species, i.e., electrons and positive holes, through the oxide layer does not control the composite growth rate.

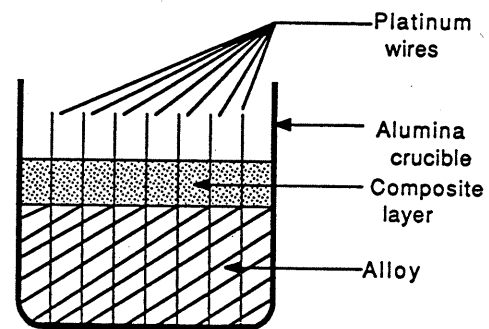


Fig. 5. Placement of the platinum wires.

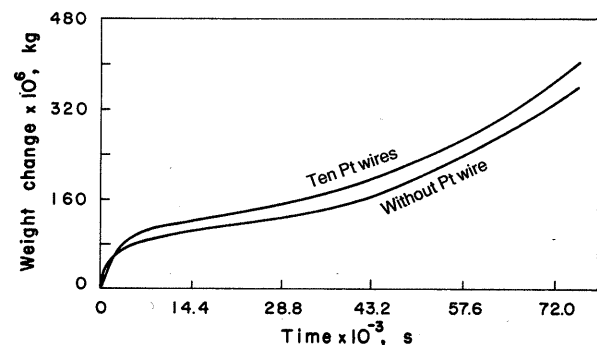


Fig. 6. Weight change vs time plots with and without the platinum wires at 1217 K.

The facts that Al_2O_3 has poor electrical conductivity in the temperature range of this investigation, and facilitation of the rates of transport of the electronic species through the oxide layer does not appreciably alter the oxidation rate, indicate two possible means of oxidation. First, if the ions are responsible for the transport of reactant species through the composite layer, movements of electronic species are essential for local charge compensation. However, if the composite is capable of providing rapid transport of electronic species, and the ionic transport is slower, further enhancement of electronic conductivity does not correspond to faster transport of electrons or holes, since the electronic transport must keep pace with the slow ionic transport to maintain charge neutrality. Second, it is possible, at least in principle, that oxygen and aluminum are not transported through the oxide layer by ionic transport. Newkirk *et al.*¹ suggested that liquid metal is transported to the surface of the ceramic layer through "wicking." The presence of narrow channels of alloy in the composite was presented as the "evidence" of the wicking process. The observation of a few alloy channels in an arbitrarily selected microscopic monitoring section does not really constitute a rigorous proof that the narrow metal channels extended from the liquid metal all the way through the ceramic oxide matrix to the top of the oxide layer. To understand the mechanism of growth, it is necessary to determine the relative importance of "wicking" and ionic diffusion. If "wicking" is important, the addition of a dopant that impairs wetting and improves ionic transport would have a detrimental effect on the growth rate. If, on the other hand, the growth rate actually improves because of the dopant addition, it would indicate the importance of ionic transport as the main mechanism for growth.

(3) Wicking vs Ionic Transport

When hole acceptors such as Zn^{2+} are present in alumina, either interstitial Al^{3+} ion or oxygen vacancy concentration in the oxide increases. Furthermore, Zn^{2+} is known to reduce the grain size of the alumina and thus enhance the grain boundary diffusion of both aluminum and oxygen ions. If the oxide of a dopant is more stable than alumina, addition of the element as a dopant would improve wetting between the alloy and the alumina matrix. However, ZnO is far less stable than Al_2O_3 and, therefore, the addition of Zn to the alloy would not significantly result in improved wetting between the alloy and the oxide matrix.²⁵ Thus, if the improved wettability and the resultant surface-tension-induced alloy transport through the oxide matrix is important for the growth of the composite, the addition of Zn to the alloy would not lead to significantly higher rate of oxidation. In Fig. 7 the rates of oxidation of an Al-Mg alloy with or without the addition of Zn are presented. It is observed that the growth rate increases significantly when Zn is added to

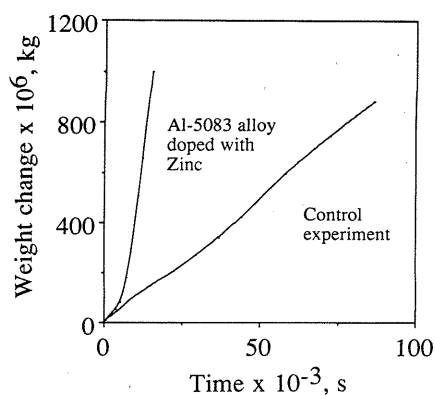


Fig. 7. Effect of zinc addition on the oxidation rate at 1294 K. Zinc granules in the amount of 0.9751 g were added to 3.9494 g of Al-5083 alloy.

the alloy. The results indicate the importance of ionic transport for the growth of the composite.

A completely different type of experiment was conducted to further examine the role of "wicking" during composite growth. A sample was soaked in argon for 1 h during the postincubation period and subsequently oxidized. If "wicking" were important, metal permeation would occur during soaking in argon and, subsequently when the crucible is exposed to air, oxidation would occur at an enhanced rate due to the presence of additional amount of liquid metal at the composite surface. Figure 8 shows the oxidation behavior of the alloy with intermittent soaking in argon. The oxidation rate immediately after argon exposure was actually lower than that immediately prior to soaking. Again, the results indicate that, after the initial period of oxidation, the "wicking" process does not control the growth rate.

Figure 9 shows a vertical midsection of a crucible containing an oxide layer and a small remaining portion of the alloy in the crucible. A void in the metal layer in the crucible indicates that the oxidation takes place at the surface of the oxide layer. This behavior is consistent with the higher ionic diffusivities of aluminum and magnesium compared to that of oxygen.

IV. Summary and Conclusions

During synthesis of ceramic oxide-based composites by directional oxidation of commercial Al-Mg alloy Al-5083, MgO forms on the surface of the alloy primarily by oxidation of magnesium vapor during the initial phase of oxidation. At 1217 K or higher, the incubation period is followed by a period of sustained oxidation after the MgO is converted to a spinel

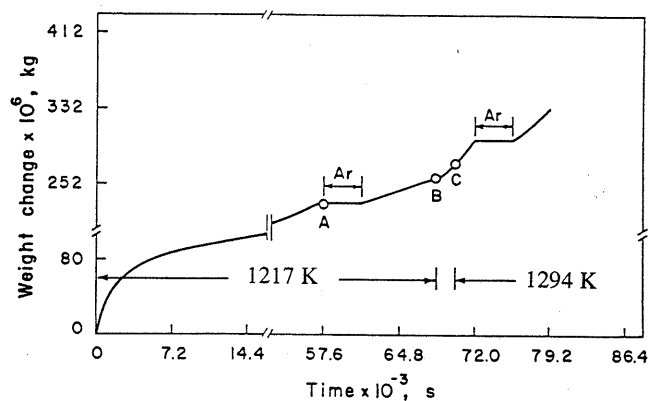


Fig. 8. Effect of inert gas exposure on the oxidation rate.

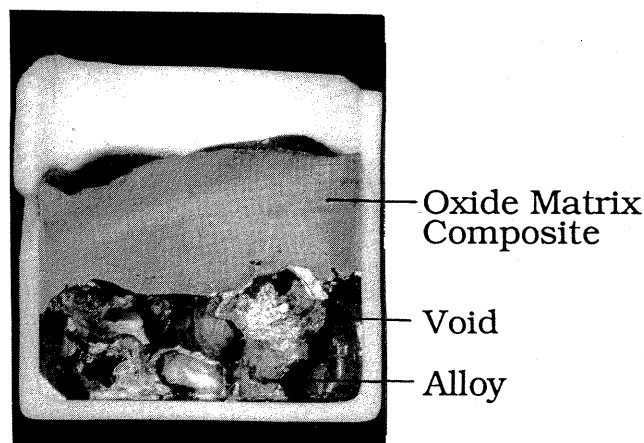


Fig. 9. Midsection of a crucible containing an oxide layer and unoxidized portion of alloy.

layer. The subsequent growth of the composite is influenced by the rate of transport of ions through the composite matrix. The oxidation rate during composite growth is not influenced by the rate of transport of the electrons and positive holes through the ceramic oxide layer.

APPENDIX

Development of Al–Mg–O Phase Diagram from the Available Thermodynamic Data

The positions of different points on the isothermal section of the Al–Mg–O phase diagram have been calculated from the available thermodynamic data.^{23,24} The positions for points A and B have been calculated from the free-energy data²⁴ in Table II and the activity data for aluminum and magnesium in Al–Mg alloys.²³

Point A



Point B



The activity coefficient of Mg has been taken as 0.88 at 1073 K. At other temperatures, the activity coefficient of Mg, γ , has been calculated assuming that the activity of Mg follows regular solution behavior in Al–Mg alloy.

$$\ln \gamma_{T_1} / \ln \gamma_{T_2} = T_2 / T_1 \quad (4)$$

The positions of points C, D, and E in Fig. 7 have been determined from stoichiometry.

Table II. Thermodynamic Data Used in the Calculations²⁴

Temp (K)	Standard free energy of formation (kJ/mol)		
	Al ₂ O ₃	MgAl ₂ O ₄	MgO
1073	–1337	–1846	–485
1173	–1304	–1802	–473
1223	–1287	–1779	–467
1273	–1271	–1757	–461
1373	–1238	–1711	–447

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